

PATENT ABSTRACTS OF JAPAN

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(54) LITHIUM BATTERY

(57)Abstract:

PROBLEM TO BE SOLVED: To provide a lithium battery which is high in stability, preserving excellent discharging characteristic at low cost, by making the electrolyte to dissolve lithium perchlorate a gel electrolyte consisting of a high polymer solid electrolyte and an organic solvent.

SOLUTION: A manganese dioxide is used for positive electrode active material, and kitchen black is used as a conductive material, and a substance where a polyethylene oxide and a functional acrylic acid ester are mixed as binders is used as a composite positive electrode 2. As the negative electrode active material of the battery, lithium metal 4 is used, and this is made to pressure contact with the negative electrode collecting plate of a stainless steel foil. For an electrolyte layer 3, a substance where γ -butyrolactone, polyethylene oxide, and function acrylic ester are dissolved with one another, and lithium perchlorate is dissolved to it is applied on the negative electrode, and it is irradiated with an electron beam to form a gel electrolyte layer. Hereby, a lithium battery high in safety can be obtained.

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CLAIMS

[Claim(s)]

[Claim 1] The lithium cell characterized by being the electrolyte presentation which is a cell using the compound which can dope a lithium metal, a lithium alloy, or a lithium as a positive electrode and a negative electrode, is the gel electrolyte with which the electrolyte which uses lithium perchlorate for a part of solute [at least], and dissolves this lithium perchlorate consists of a solid polymer electrolyte and an organic solvent, and is the concentration which lithium perchlorate can dissolve in a giant-molecule solid electrolyte even if it removes this organic solvent.

[Claim 2] The lithium cell according to claim 1 with which said giant-molecule solid electrolyte contains polyethylene oxide.

[Claim 3] The lithium cell according to claim 1 said whose organic solvent is gamma-butyrolactone.

DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Field of the Invention] This invention relates to amelioration of a lithium cell.

[0002]

[Description of the Prior Art] In recent years, electronic equipment is miniaturized with development of the electronics field, and a miniaturization is desired like electronic equipment also in the cell. The cell using especially the lithium as a negative-electrode active material is a cell which is small and can expect high capacity from a high energy consistency being expectable.

[0003] However, on the occasion of utilization of a lithium cell, safety has been a very important technical problem. That is, a lithium reacts violently with the moisture in air or water, and alcohols, and igniting is known. The active state of a lithium appeared in the rechargeable battery which performs charge and discharge especially, the rocking chair type cell using the carbon which doped the lithium ion as the cure was devised also from it being risk, and it has resulted in utilization. However, also in these cells, the negative electrode in the end of charge is activity, and has the same reactivity as a lithium.

[0004] Therefore, in current, since various safety practices are studied from the field of a solvent, a solute, an active material, etc. and it supplements with own safety of a cell, it is

carrying out establishing a protection network in the cell exterior etc.

[0005] In the point of the safety in an electrolyte, development of a solid electrolyte system is performed positively. Since the solid electrolyte is superior to the inorganic electrolyte in ionic conductivity and a processing side, the organic solid polymer electrolyte serves as the object for central research. Since this kind of electrolyte is not evaporated in an elevated temperature, extreme lifting of the cell internal pressure to a temperature rise is not generated. However, since the ionic conduction of a solid polymer electrolyte below ordinary temperature is inadequate, high power can tell utilization that there are many problems for the application for which the output in the need or low temperature is needed.

[0006] Moreover, especially as for the lithium salt used for an electrolyte, lithium perchlorate has been used as an object for primary cells. It is the reason that lithium perchlorate is cheap and ionic conductivity is high. However, exploding, if the crystal of lithium perchlorate is unstable and heat and an impact are given is known.

[0007]

[Problem(s) to be Solved by the Invention] This invention is made in view of the above-mentioned trouble, and as long as it is used within the limits of the operation decided though the outstanding discharge property was held, it aims at offering a lithium cell with high safety cheaply.

[0008]

[Means for Solving the Problem] In the cell using the compound which can dope a lithium metal, a lithium alloy, or a lithium as a positive electrode and a negative electrode, it becomes possible by using lithium perchlorate for a part of solute [at least] to acquire good ionic conduction in a large temperature range. As mentioned above, lithium perchlorate is dramatically dangerous if heat and an impact are given in the condition of having not dissociated. However, it is the gel electrolyte with which the electrolyte which dissolves lithium perchlorate consists of a solid polymer electrolyte and an organic solvent. When it is the electrolyte presentation which is the concentration which lithium perchlorate can dissolve in a solid polymer electrolyte even if it removes this organic solvent, Even if the organic solvent with which a cell is put with the misuse besides the safety standard in a cell on the bottom of an elevated temperature (before or after 100 **), and a relief valve constitutes some aperture gel electrolytes from superfluous vapor pressure of the electrolytic solution evaporates Since it is spread as ion to the polymer which can dissolve lithium salt, the deposit as a crystal of lithium perchlorate does not take place. Since the molecular motion of a polymer especially becomes large in an elevated temperature, it is thought that it resulted in preventing a segregation. Moreover, when the giant-molecule solid electrolyte contained in the electrolyte in a gel electrolyte is polyethylene oxide, it is possible to incorporate a lithium ion and an anion promptly. Although polyvinyl alcohol etc. dissolves a salt well, since problems with a lithium, such as reactivity, are mentioned, it can be said that polyethylene oxide is desirable. Considering that the lithium ion in the inside of polyethylene oxide serves as ligand, is carried out 4 coordination, and the oxygen atom is dissolving it, generally the maximum solubility has 0.25 dissolutions possible for a lithium ion to an oxyethylene unit. However, since it is greatly influenced according to the molecular weight of the polymer to be used or structure, and charge distribution including the solid polymer electrolyte of the structure which does not contain an oxyethylene unit, it is not limited to this.

[0009] Moreover, if a hypoviscosity solvent is used, the property in low temperature will improve, but since the safety under an elevated temperature has the quick volatilization rate of a solvent, it falls to reverse. the propylene carbonate generally used -- if independent, since the property in low temperature is bad, it is desirable that the organic solvent contained in an electrolyte is gamma-butyrolactone.

[0010] It is a cell using the compound which can dope a lithium metal, a lithium alloy, or a lithium as a positive electrode and a negative electrode as above-mentioned. It is the gel electrolyte with which the electrolyte which uses lithium perchlorate for a part of solute [at least], and dissolves this lithium perchlorate consists of a solid polymer electrolyte and an organic solvent. Even if it removes this organic solvent, as long as it is used within the limits of the operation decided though the discharge property which was cheap and was excellent by being the electrolyte presentation which is the concentration which lithium perchlorate can dissolve in a solid polymer electrolyte was held, offer of a lithium cell with high safety is attained. Moreover, when the giant-molecule solid electrolyte contained in an electrolyte contains polyethylene oxide, a lithium cell with more high safety can be offered. In addition, the manifestation of the outstanding cell property in a large temperature range of the organic solvent contained in an electrolyte is attained by being gamma-butyrolactone.

[0011]

[Embodiment of the Invention] Hereafter, although an example explains the detail of this invention, this invention is not limited to this.

[0012] (This invention) The sheet-like cell of this invention was produced according to the following procedure. That a positive-active-material layer should be formed, the manganese dioxide was used for positive active material, and what mixed KETCHIEN black as electric conduction material, and mixed polyethylene oxide 2 organic-functions acrylic ester as a binder was used as a compound positive electrode. The production approach is as follows. the above-mentioned organic compound and gamma-butyrolactone are dissolved in 15g of things which mixed KETCHIEN black with the manganese dioxide by the weight ratio of 10:1 so that an organic compound may become 50% with volume percentage -- making -- lithium perchlorate -- 0.6 mols/l. what was dissolved so that it might become -- 4g -- adding -- mixing -- a positive electrode -- it considered as the mixture. the positive electrode above-mentioned to the stainless steel foil top which is a positive-electrode charge collector -- after carrying out the cast of the mixture, the electron ray was irradiated and it considered as the positive electrode.

[0013] This was stuck to the negative-electrode collecting electrode plate of a stainless steel foil by pressure, using a lithium metal as a negative-electrode active material of a cell. Polyethylene oxide 2 organic-functions acrylic ester is dissolved in gamma-butyrolactone so that it may become 50% with volume percentage, and electrolyte layers are lithium perchlorate 0.6 mol/l After applying what was dissolved on an above-mentioned negative electrode so that it may become, the electron ray was irradiated and the gel electrolyte layer was made to form.

[0014] After piling up the positive electrode / electrolyte / lithium produced as above-mentioned and having arranged the frame made from denaturation polyethylene in the obturation section, thermal melting arrival was carried out by the heat sealer, and the sheet-like cell was produced. In addition, the valve opened by internal pressure lifting by laser marking was prepared in the positive-electrode side of a cell charge collector.

[0015] Drawing 1 is the sectional view of the thin form cell of this invention. One in drawing is the positive electrode and negative-electrode charge collector which consist of stainless steel which served also as sheathing, and 2 is positive-electrode plied timber which used the manganese dioxide as the active material. It is the obturation material which an electrolyte becomes in 3 and a metal lithium and 5 become from denaturation polyethylene in 4.

[0016] (Example of a comparison) The sheet-like cell of the example of a comparison was produced according to the following procedure. That a positive-active-material layer should be formed, the manganese dioxide was used for positive active material, and what mixed KETCHIEN black as electric conduction material, and mixed polyethylene oxide 2 organic-functions acrylic ester as a binder was used as a compound positive electrode. The production approach is as follows. the mixed solvent of the volume ratio 3:2 of the above-mentioned organic compound, propylene carbonate, and dimethoxyethane is dissolved in 15g of things which mixed KETCHIEN black with the manganese dioxide by the weight ratio of 10:1 so that an organic compound may become 40% with volume percentage -- making -- lithium perchlorate -- 0.6 mol/l what was dissolved so that it might become -- 4g -- adding -- mixing -- a positive electrode -- it considered as the mixture. the stainless steel foil top which is a positive-electrode charge collector -- this positive electrode -- after carrying out the cast of the mixture, the electron ray was irradiated and it considered as the positive electrode.

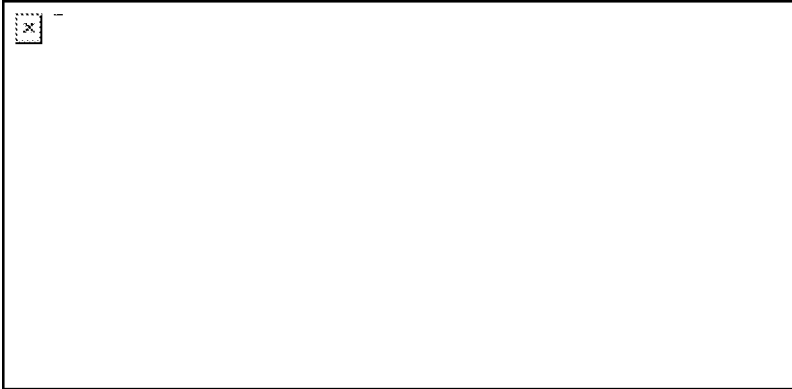
[0017] This was stuck to the negative-electrode collecting electrode plate of a stainless steel foil by pressure, using a lithium metal as a negative-electrode active material of a cell. An electrolyte layer is 0.6 mols/l. about lithium perchlorate to the mixed solvent of 3:2 at the volume ratio of propylene carbonate and dimethoxyethane. Impregnation of what was dissolved so that it might become was carried out to the nonwoven fabric, and the electrolyte layer was made to form.

[0018] After piling up the positive electrode / electrolyte / lithium which the **** produced and having arranged the frame made from denaturation polyethylene in the obturation section, thermal melting arrival was carried out by the heat sealer, and the sheet-like cell was produced. In addition, the valve opened by internal pressure lifting by laser marking was prepared in the positive-electrode side of a cell charge collector like this invention.

[0019] Above-mentioned this invention and the cell of the example of a comparison were carried on the hot plate with which skin temperature is beforehand maintained at 120 **, and change of the cell to time amount was observed. The result is shown in a table 1.

[0020]

[A table 1]



[0021] [in time amount progress 10 minutes], as for the cell of the example of a comparison, internal pressure rose, and, as for the cell of this invention, change was not accepted to a configuration no longer being maintained so that clearly from a table 1. This is considered to be the difference in whether the dimethoxyethane which is a low-boiling point solvent is in close. The relief valve opened all the cells of the example of a comparison in time amount progress 11 - 20 minutes. Moreover, the relief valve opened the cell of this invention altogether in about 21 - 30 minutes. It is thought that this difference is a thing resulting from the difference in an electrolyte. Then, what explodes in about 21 - 30 minutes generated the cell of the example of a comparison about 60%. On the other hand, even if the cell of this invention passes through progress of 40 minutes, a burst is 0%, and it was only about 5% which explodes even if it passes through 3 passage of time.

[0022]

[Effect of the Invention] It is the gel electrolyte with which the electrolyte which dissolves lithium perchlorate also in the cell using the ***** lithium perchlorate which is [like] dangerous from the above explanation consists of a solid polymer electrolyte and an organic solvent, and even if it removes this organic solvent, when the giant-molecule solid electrolyte contained in an electrolyte contains polyethylene oxide again, a lithium cell with more high safety can be offered by being the electrolyte presentation which is the concentration which lithium perchlorate can dissolve in a solid polymer electrolyte. In addition, the organic solvent contained in an electrolyte is gamma. - As long as it is activity within the limits for which it opted though the discharge property which the manifestation of of the outstanding cell property in a large temperature range was attained, as a result was excellent by being a butyrolactone was held and is used, the effectiveness that it is cheap and the lithium cell which raised safety design can be offered is done so.

DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the sectional view of the lithium cell of this invention.

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